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(54) Title: 3-LAYER TUBE FORMING APPARATUS

(57) Abstract

A gaseous diffusion resistant tube comprising an inner core of a heat resistant polymeric material, typically cross-linked polyethylene, protected outer layer of impact resistant material and an intermediate layer of non-metalliferous gaseous diffusion resistant material characterised in that the intermediate layer is bonded to at least one of the inner core and the outer layer by bonding material compatible with each of the materials to be bonded and is sufficiently elastic that it will not delaminate or rupture either itself or the adjoining layer under heat cycling conditions. In a preferred embodiment of the invention, the bonding material is preferably a material different to the layer to which it bonds. The invention also discloses apparatus for carrying the invention into effect.

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"3-LAYER TUBE FORMING APPARATUS"

DESCRIPTION

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British Patent Specification No. 1,158,011 describes and claims a method of forming a cross-linked material which comprises subjecting a cross-linkable material to a plurality of instantaneous compressions at a pressure greater than 2,000 atmospheres to raise the temperature of the material to a level just below the threshold which crosslinking of the material takes place, forming or shaping of the material and thereafter causing or allowing crosslinking of the material to occur. Material produced in accordance with Patent No. 1,158,011 has been found to be an excellent material for use in the piping of hot water and materials generally having a temperature not above 120°C and not being a solvent for the particular crosslinked polyclefin. In particular, cross-linked polyethylenic material formed in accordance with

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Patent No. 1,158,011 has been found excellent in use for a large number of years.

5 With the advent of more rigorous operating conditions,
a demand has risen for a gaseous diffusion resistant
plastics tube otherwise having the properties of the
crosslinked material produced in accordance with
British Patent No. 1,158,011 referred to above. Many
proposals have been put forward and typical of them
10 are proposals to include a layer of metal foil bonded
to the crosslinked polyolefinic material either on a
surface thereof or bonded as an intermediate layer
therein. This solution suffers from the disadvantage
that while the initial construction works well,
15 continued heat cycling produces eventual delamination
of the foil layer from the adjacent layers within the
tube and/or produces cracks or splits. The effect of
delamination and/or cracks or splits is to allow once
again the passage of gas through the material via the
20 breaks and/or the splits in the material itself. This
has been a problem that has been long known in the
construction of, for example, telephone cables and
many attempts have been made to overcome it. The
solutions for telephone cables are not, however,
25 compatible in this particular case, since the

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continual heat cycling of tube used in a heating system whereby the temperature of the tube is continuously alternating between hot and cold, produces a more rigorous environment. The basic problem is that the differential expansion between the core material of the tube and the material constituting the gaseous diffusion resistant layer has to be such that the integrity of each and the bonding of one to the other is maintained.

United States Patent Specification No. 3,561,493 describes a composite tube comprising two or more layers in which each discrete layer is conjoined with its neighbour by means of a jointing layer composed by mixtures of the two constituent plastics which separately form the discrete layers to be conjoined. While such a construction may be acceptable in terms of mechanical strength and ageing resistance, it is not per se suitable in circumstances where repeated temperature eyeing occurs since shear forces are generated which lead to delamination of such composite tubes.

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In our European Patent Application No. 80304008.8 we have described a multi-layer gaseous diffusion resistant plastics tube comprising a core of a liquid resistant plastics material, and an outer layer of a plastics impact resistant material, characterised by a continuous intermediate layer of a gaseous resistant material interposed between, and bonded to both the core and the outer layer. It is described as being produced by sequential co-extrusion of the layers for fusion at their abutting interfaces. Because at least the core, and usually the core and the outer layer, of such three-layered tubes are formed of a cross-linkable or thermoset material, and because the extrusion coincides with the cross-linking or thermosetting step, the co-extrusion of the three-layer tube requires both a long process line and slow moving formation.

The process of our co-pending European Application can be enhanced by using an intermediate layer of non metalliferous gaseous resistant material which is bonded in such a way that there is complete continuity between the adjacent layers and the intermediate gaseous resistant layer.

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We have now found that an improved product of this type can be produced by using as a core, a fully cured or cross-linked material, and subsequent bonding layers which substantially eliminate discontinuities therein; such for example as may occur with the inclusion of small air bubbles trapped between the intermediate layer and the inner or outer layer.

According to the present invention, there is provided

10 a gaseous resistant tube comprising
 an inner core of a heat resistant polymeric material,
 a protective outer layer of an impact resistant material, and
15 an intermediate layer of a non metalliferous gaseous resistant material
 characterised in that the intermediate layer is bonded to at least one of the inner core and to the outer layer by a bonding material compatible with each of
20 the materials to be bonded and is sufficiently elastic that it will not delaminate or rupture either itself or the adjoining layer under heat cycling conditions.

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The intermediate layer may be any gaseous resistant plastics material bondable with both the inner core and the outer layer. The bonding means may be a priming layer and/or adhesive layer to assist bonding.

5 The bonding means is preferably a priming layer and/or adhesive layer dissimilar to the material to be bonded where both a priming layer and an adhesive is employed at least one should be dissimilar to the material of adjacent layer to be bonded. A typical construction is

10 the use of a polyvinyl alcohol as a gaseous resistant layer having a priming layer of polyurethane and a thin layer of polyethylene applied thereto to assist bonding to a crosslinked polyethylenic inner core and a graft polyethylene copolymer with a silane or a like

15 material having high impact resistance as the outer layer.

The invention may also include a method of forming a gaseous resistant tube which method comprises

20 preheating a tube core material to a temperature of at least 60°C, wrapping an intermediate layer of gaseous resistant material bondable to said core about said preheated core material to produce a longitudinal overlap, heat-sealing said overlap longitudinally of

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said core and extruding an outer layer about said material under conditions of heat and pressure such that any gaseous matter in the interface between the core and intermediate layer is removed therefrom and such that bonding between the core and the intermediate layer and the outer layer takes place. At this stage, heat may be applied to the core and/or to the core and intermediate layer before the extrusion. The intermediate layer is preferably biaxially stretched and heat shrinkable, the arrangement being such that on extrusion of the outer layer thereabout the intermediate layer is caused to shrink about the core and the sensible heat of the extruded outer layer serves to effect bonding between the intermediate layer of the core and the intermediate layer in the outer layer while the pressure applied during the extrusion step is sufficient to complete the bonding and to squeeze or drive out air bubbles which may otherwise occur between the intermediate layer and one or both of its adjacent layers.

A typical intermediate layer may comprise a layer of polyvinyl alcohol in the form of film having a thickness of 0.01 to 0.06 mm, a priming coat of

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polyurethane on each surface thereof at a thickness of the order of 0.3 to 3.0 grams per square metre to act as primer and a compatible glue layer of polyethylene provided to each primed surface having a
5 thickness of the order of 0.025 to 0.035, preferably 0.030 mm in thickness. The intermediate foil is preferably biaxially stretched so that it shrinks on heating.

10 The invention includes a method for the manufacture of tubes in accordance with the invention, which method comprises extruding an inner core of heat resistant polymeric material supplying a laminate of a non metaliferous gaseous resistant layer with bonding
15 material carried thereon and wrapping said laminate about said inner core unsupported by an internal mandrel,

and extruding a protective outer layer of an impact resistant material over the exposed surface of
20 said intermediate layer,

characterised in that the bonding material is a material different from each of the materials to which it bonds and in that the conditions of heat and pressure of the extrusion step is such as to expel air
25 and to effect bonding between the adjacent layers

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whereby the finished tube will not delaminate or rupture any layer under heat cycling conditions.

In another aspect of the invention there is provided
5 an apparatus for the formation of a three-layer plastics tube, which comprises:

core supply means for supplying a cross-linked core to a first forming station adapted to form an intermediate layer about said core,

10 extrusion means adapted to extrude an outer layer about the formed intermediate layer and to fix the same thereabout, and

cooling and make-up means to store the so-formed product.

15 The apparatus may include a heating station for heat the core prior to supply of the core to the first forming station.

20 In another embodiment, the product formed is substantially as described in our co-pending European Application referred to above; in which case the core is formed of a cross-linked polyolefin, preferably cross-linked polyethylene. However, other cross-linked

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plastics materials, well known to those in the art, are also suitable for particular purposes.

5 In another embodiment a further layer may be formed and/or bonded with the core and the intermediate layer may be formed thereover. Similarly the outer core may be of a multilayer construction.

10 Similarly, there are a number of well known thermosetting materials which may equally be extruded to tubular form about the core/intermediate layer preform and heat-set to give a hardened tubular core material.

15 The intermediate layer and outer layer are most preferably selected such that their coefficients of heat expansion in their formed condition are much the same, and the same as the core material. Thus, the core and the outer layers may be selected from
20 cross-linked polyolefinic materials, particularly cross-linked polyethylene, while the intermediate layer may be a material such as polyvinyl alcohol (PVAL EVAL, and PA). Indeed, in some situations a polyethylene coated aluminium foil can be used as the
25 intermediate layer if the coefficients of expansion of

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the core and the outer layers are adjusted accordingly to reduce or eliminate heat shear on heat cycling.

5 As in the above-mentioned European Patent Application, the core material may be selected only for its inertness to the intended fluid of use in the bore of the core, the intermediate layer may be selected only for its gaseous diffusion resistant properties, while the outer layer may be selected only on the basis of
10 its resistance to impact, with the provision that the three materials selected must be fusible at their interfaces with, or without the use of adhesives.

The outer layer is usually selected in part at least
15 for its heat impact and chemical resistance. A suitable material for the outer layer may be Sioplas E (Registered Trade Mark) or any standard-free radical initiated cross-linked polyolefin.

20 The bonding means in accordance with the invention may be applied between only one of the layers. Thus, in the case where the core is of cross-linked polyethylene, and where PVA1 is the intermediate layer heat and pressure alone can be utilized to bond the
25 intermediate layer to the core. Where the outer layer

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is of Sioplas E the heat of extrusion of cross-linking can be utilized to fuse the other layer to the intermediate layer but in this case the outer surface of the PVA1 layer is primed with polyethylene as an adhesive.

If the temperature for forming the various layers are correctly inter-related, the overall heat input can be reduced by utilizing any exothermic reactions generated in the cross-linking reactions to bond not only the outer layer to the intermediate layer, but also the intermediate layer to the core.

Thus, in a preferred embodiment of the invention a core of cross-linked polyolefin or similar material is preheated and a film of PVA1 or similar material carrying the necessary bonding layer(s) is formed thereover in longitudinal overlapping relation, the overlap being heat and/or pressure sealed to secure the intermediate in its correct orientation about the core along an axial line. This has the benefit of enhancing the diffusion resistance of the construction to gas. The resultant core/intermediate layer preform is then fed to an extruder head and the outer material such as Sioplas E is coextruded thereabout in a

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continuous layer. The heat and pressure from this co-extrusion not only fuses the outer layer to the intermediate layer, but also the intermediate layer to the inner core.

5

Alternatively, the intermediate and core layers may be fully bonded prior to the application of the outer layer if desired.

10

A suitable material for forming the outer layer which may also include pigment, is a graft copolymer of polyethylene with a silane. In such a process raw polyethylene granules are admixed with vinyl trimethoxy silane (VTMOS) and a peroxide to form a

15 graft copolymer. The graft copolymer when heated (for example during extrusion) in the presence of a catalyst such as dibutyltin dilaurate forms a suitable high impact heat and stress-cracking resistant polymer for use as the outer layer of the three-layer product.

20

Coloured elongate strips may be applied by a suitably positioned extruder, and heat extruding a strip of the desired material onto the outer periphery of the outer layer.

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The invention will now be described, by way of illustration only, with reference to the accompanying drawing which shows, in diagrammatic plan view, an extrusion apparatus of the present invention.

5

With reference to the drawing, there is provided a supply reel 1 of generally known type disposed on a stand and adapted to unwind a supply of cross-linked polyethylene tube hereinafter referred to as "pex" tube. The pex tube may then pass a preheater which heats the surface of the core to facilitate bonding to the PVAL laminate.

10

Indicated generally at 4 is a polyvinyl alcohol laminate the laminate 4 and the pex tube 2 being fed to a centering device 3 which acts both to form the laminate 4 about the pex tube and to centre so-formed layers relative to the extrusion apparatus. The polyvinyl alcohol laminate comprises an intermediate layer of polyvinyl alcohol with a surface coating of polyethene for juxtapositioning with the pex core.

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The heated preform is then fed to a shaping device 6 and welding device 7 sequentially. At the shaping device 6 the laminate 4 is formed into a longitudinal

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overlapping relation upon the pex tube 2 and welded thereto in welding means 7 by the application of axially applied heat and pressure to the seam thereformed. The heat applied should be sufficient to
5 raise the temperature of the pex tube and/or the laminate surface at or towards their melting points and the pressure should be such as to expel air and effect bonding. The heat and pressure can be effected using a fluid with a high boiling point and under
10 hydrostatic pressure, i.e. a molten salt bath or a molten metal bath.

Infra-red radiation and laser bonding may be used, instead of or in addition to, applied heat.

15

The so-formed preform is then fed to extrusion head 8 wherein a continuous layer of Sioplas E is coextruded thereupon, both to form continuous outer layer of impact resistant material to expel any air inclusions,
20 and to heat the preform to a temperature at which fusing of both the outer layer and intermediate layer, and the intermediate layer core layer interfaces are assured.

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The so-formed three-layer product, on passing from the extruder 8 is fed to a cooling bath 10. There is a spatial distance between the extrusion head 8 and the cooling bath 10 which is adjustable so as to allow a sufficient time for the fusing and cross-linking reactions to proceed to their completion. The spatial distance is a function of the speed of the process line and the speed of the reaction, which is governed by the temperature which can be attained at the extrusion head.

The formed product 15 is then led over a guide 13 and taken up on a take up reel (not shown).

By use of the apparatus in accord with the present invention the three-layer product can be formed some five to ten times faster than the production of the core tube alone, and considerably faster than the case where coextrusion is utilized.

Following is a description by way of example only of one method of carrying the invention into effect.

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Example

A tube formed of crosslinked polyethylene produced generally in accordance with Patent No. 1,158,011 having an outside diameter of 19.5 mm and a wall thickness of 1.7 mm was heated to a temperature of 70°C. Using the apparatus described with reference to Figures 1 and 2 of the accompanying drawings, a commercial foil laminate was then applied to the preheated crosslinked polyethylene core. The foil in the form of a longitudinal sheet was a biaxially stretched polyvinyl alcohol foil having a thickness of 0.015 mm having a priming layer of polyurethane on either side thereof at a coating weight of 0.5 gram per square metre and carrying a bonding layer of polyethylene having a thickness of 0.03 mm. The foil had a total thickness, therefore, of 0.075 mm. The foil was then wrapped longitudinally as described above and sealed with an overlap of about 5 mm. A heating shoe was then applied to the overlap, the temperature of the shoe being approximately 145°C. A graft copolymer of polyethylene with silane was prepared by mixing polyethylene granules with vinyl trimethoxysilane and a peroxide to form a graft copolymer. A proportion of a catalyst dibutyltin

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dilaurate was then added so that on heating, the graft copolymer was capable of being extruded and exposure of the material on cooling would cause or allow crosslinking of the material to take place thereby forming a high impact protective outer layer. The graft copolymer was then heated to a temperature of about 170°C and extrusion of the material was proceeded with at a pressure of about 100 atmospheres in order to effect shaping of the material about the core and intermediate layer contained thereby. The temperature of the graft copolymer as extruded together with the pressure applied was sufficient:-

1. to expel any air between the graft copolymer and the intermediate layer and the intermediate layer and the core, while the temperature was sufficient;
2. to cause the intermediate layer to shrink due to its biaxial prestretch;
3. sufficient to cause bonding between the core of polyethylene coated in the intermediate layer adjacent thereto and between the graft copolymer of polyethylene coating on the outer surface of the intermediate layer to produce an a unitary construction having a consistant and continuous layer

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of gaseous resistant material, in this case polyvinyl alcohol extending within the wall of the tube.

5 The presence of air and moisture is sufficient to cause the graft copolymer to crosslink and once the crosslinking reaction has proceeded to completion, the outer layer acquires the properties of high impact outer cover.

10 Tubes formed in the manner described above have been found to provide excellent resistance to gaseous diffusion within the tube, and tubing produced in this way has excellent longevity.

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CLAIMS

1. A gaseous resistant tube comprising
an inner core of a heat resistant polymeric
material,
a protective outer layer of an impact
resistant material, and
an intermediate layer of a non metalliferous
gaseous resistant material
characterised in that the intermediate layer is bonded
to at least one of the inner core and to the outer
layer by a bonding material compatible with each of
the materials to be bonded and is sufficiently elastic
that it will not delaminate or rupture either itself
or the adjoining layer under heat cycling conditions.
2. A tube as claimed in claim 1 characterised in
that the core material is cross-linked polyethylene.
3. A tube as claimed in claim 1 or claim 2
characterised in that the intermediate layer is
selected from polyvinyl alcohol, ethylvinyl alcohol
and polyacrylonitrile.

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4. A tube as claimed in any preceding claim characterised in that the bonding material is a different material to the material of the layer to which it bonds.

5

5. A tube as claimed in any preceding claim characterised in that the bonding material is selected from one or more of polyurethane, polyethylene, and hot melt.

10

6. A tube as claimed in any preceding claim characterised in that the intermediate layer is biaxially stretched.

15

7. A method for the formation of a tube as claimed in claim 1 which method comprises extruding an inner core of heat resistant polymeric material supplying a laminate of a non metaliferous gaseous resistant layer with bonding material carried thereon and wrapping said laminate about said inner core unsupported by an internal mandrel,

20

and extruding a protective outer layer of an impact resistant material over the exposed surface of said intermediate layer,

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characterised in that the bonding material is

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a material different from each of the materials to which it bonds and in that the conditions of heat and pressure of the extrusion step are such as to expel air and to effect bonding between the adjacent layers whereby the finished tube will not delaminate or
5 rupture any layer under heat cycling conditions.

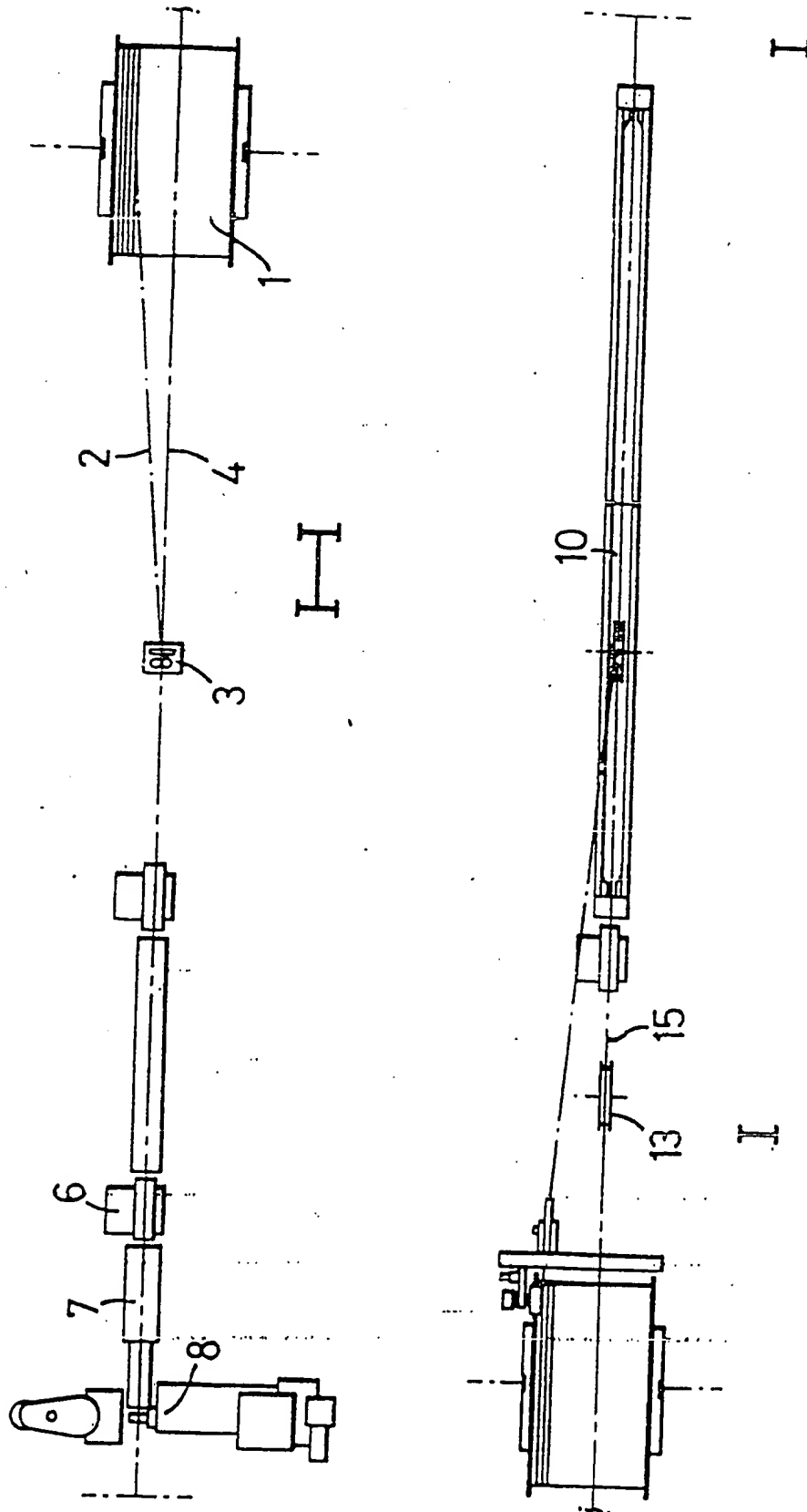
8. A method as claimed in claim 7 characterised in that the wrapping is conducted to produce a
10 longitudinal overlap and heat and pressure is applied to weld the joint.

9. A method as claimed in claim 7 or claim 8 wherein the outer layer comprises a graft copolymer of
15 polyethylene with vinyl trimethoxysilane.

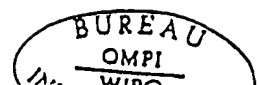
10. A method as claimed in any one of claims 7 to 9 wherein the extrusion is conducted at a pressure of at least 80 atmospheres and a temperature of at least
20 160°C.

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INTERNATIONAL SEARCH REPORT

International Application No PCT/EP 83/00296

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ¹ According to International Patent Classification (IPC) or to both National Classification and IPC IPC ³ : F 16 L 9/12																	
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched ⁴</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 20%; border-bottom: 1px solid black;">Classification System</td> <td style="border-bottom: 1px solid black;">Classification Symbols</td> </tr> <tr> <td style="padding: 5px;">IPC³</td> <td style="padding: 5px;">F 16 L</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵</div>			Classification System	Classification Symbols	IPC ³	F 16 L											
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III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴ <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%; padding: 5px;">Category ⁶</th> <th style="width: 60%; padding: 5px;">Citation of Document, ¹⁵ with Indication, where appropriate, of the relevant passages ¹⁷</th> <th style="width: 30%; padding: 5px;">Relevant to Claim No. ¹⁸</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">X</td> <td style="padding: 5px;">EP, A, 0030091 (SKARELIUS) 10 June 1981 see claims 1-11; figures 1,2 cited in the application</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-4</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">X</td> <td style="padding: 5px;">CH, A, 436692 (TUBOPLAST-FRANCE S.A.) 15 November 1967 see column 1, lines 20-22; column 2, lines 7-18</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-4,7</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">X</td> <td style="padding: 5px;">GB, A, 1108136 (BRISTOL AEROPLANE PLASTICS) 3 April 1968 see page 1, lines 66-80; claims 1-9</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-4,7,8</td> </tr> <tr> <td colspan="3" style="text-align: center; padding: 5px;">-----</td> </tr> </tbody> </table>			Category ⁶	Citation of Document, ¹⁵ with Indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸	X	EP, A, 0030091 (SKARELIUS) 10 June 1981 see claims 1-11; figures 1,2 cited in the application	1-4	X	CH, A, 436692 (TUBOPLAST-FRANCE S.A.) 15 November 1967 see column 1, lines 20-22; column 2, lines 7-18	1-4,7	X	GB, A, 1108136 (BRISTOL AEROPLANE PLASTICS) 3 April 1968 see page 1, lines 66-80; claims 1-9	1-4,7,8	-----		
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>[*] Special categories of cited documents: ¹³</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the International filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"PP" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"Δ" document member of the same patent family</p> </div> </div>																	
IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;">Date of the Actual Completion of the International Search ¹</td> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;">Date of Mailing of the International Search Report ¹</td> </tr> <tr> <td style="text-align: center; padding: 5px;">2nd February 1984</td> <td style="text-align: center; padding: 5px;">29 FEB. 1984</td> </tr> <tr> <td style="border-bottom: 1px solid black; padding: 5px;">International Searching Authority ¹</td> <td style="border-bottom: 1px solid black; padding: 5px;">Signature of Authorized Officer ¹⁹</td> </tr> <tr> <td style="text-align: center; padding: 5px;">EUROPEAN PATENT OFFICE</td> <td style="text-align: center; padding: 5px;"> G.L.M. Krüdenberg </td> </tr> </table>			Date of the Actual Completion of the International Search ¹	Date of Mailing of the International Search Report ¹	2nd February 1984	29 FEB. 1984	International Searching Authority ¹	Signature of Authorized Officer ¹⁹	EUROPEAN PATENT OFFICE	 G.L.M. Krüdenberg							
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EUROPEAN PATENT OFFICE	 G.L.M. Krüdenberg																

ANNEX TO THE INTERNATIONAL SEARCH REPORT

INTERNATIONAL APPLICATION NO. PCT/EP 83/00296 (SA 5995)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 21/02/84

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A- 0030091	10/06/81	JP-A- 56127441 CA-A- 1145272	06/10/81 26/04/83
CH-A- 436692		None	
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